

Analysis of Amphibole Asbestiform Fibers in Municipal Water Supplies

by William J. Nicholson*

Details are given of the techniques used in the analysis of asbestiform fibers in the water systems of Duluth, Minnesota and other cities. Photographic electron diffraction and electron microprobe analyses indicated that the concentration of verified amphibole mineral fibers ranged from 20×10^6 to 75×10^6 fibers/l. Approximately 50-60% of the fibers were in the cummingtonite-grunerite series and 20% were in the actinolite-tremolite series. About 5% were chemically identical with amosite. A wide variety of analytical techniques must be employed for unique identification of the mineral species present in water systems.

Asbestos is a generic term applied to a variety of commercially useful fibrous silicate minerals capable of withstanding high temperatures and relatively resistant to acid and alkaline solutions. The minerals include chrysotile, in the serpentine group, and amosite, crocidolite, tremolite, anthophyllite, and actinolite in the amphibole group.

Approximately 95% of asbestos production and use in the United States involves chrysotile fibers. Improper disposal of waste chrysotile during mining, manufacturing, or primary and secondary use can contaminate public water supplies. This contamination may, in addition, be supplemented by erosion from natural deposits of serpentine minerals found in many parts of the United States (1). Because of the extensive use of chrysotile, most attention has focussed on this mineral as a potential water contaminant. While only minor commercially usable deposits of tremolite and anthophyllite exist in the United States, amphibole minerals are, however, more plentiful and more widely distributed than those of the serpentine group. In fact, they may comprise as much as 5% of the earth's crust and upper mantle (2). Thus, con-

tamination of public water supplies by fibrous amphibole minerals must also be considered.

A classic example of such contamination of public water by amphibole minerals can be found in the tailings discharge of an iron ore mining company located at Silver Bay, Minnesota. The company discharges approximately 70,000 tons of tailings daily into Lake Superior. The discharge is the residue from the processing of taconite ore, originally mined at Babbitt, in the Mesabi Range, into pellets at Silver Bay for shipment to steel mills. The tailings are predominantly in the cummingtonite-grunerite mineral series with the nominal chemical formula, $\text{Fe}_x \text{Mg}_y \text{Si}_8\text{O}_{22}(\text{OH})_2$, where $x + y = 7$ in the idealized case. This amphibole mineral series is a continuous one, varying only in the relative percentages of iron to magnesium. The transition between cummingtonite and grunerite is considered to occur at $x/(x + y) = 0.70$. It is interesting to note that the asbestos mineral amosite is, in fact, a grunerite mineral, with a value of $x/(x + y)$ of about 0.77 (3).

Figure 1 shows a transmission electron photomicrograph of this tailings discharge. A multitude of fibers are present, ranging in size from fibers having diameters exceeding $1 \mu\text{m}$ to fibers as thin as perhaps 500 Å. Figures 2 and 3

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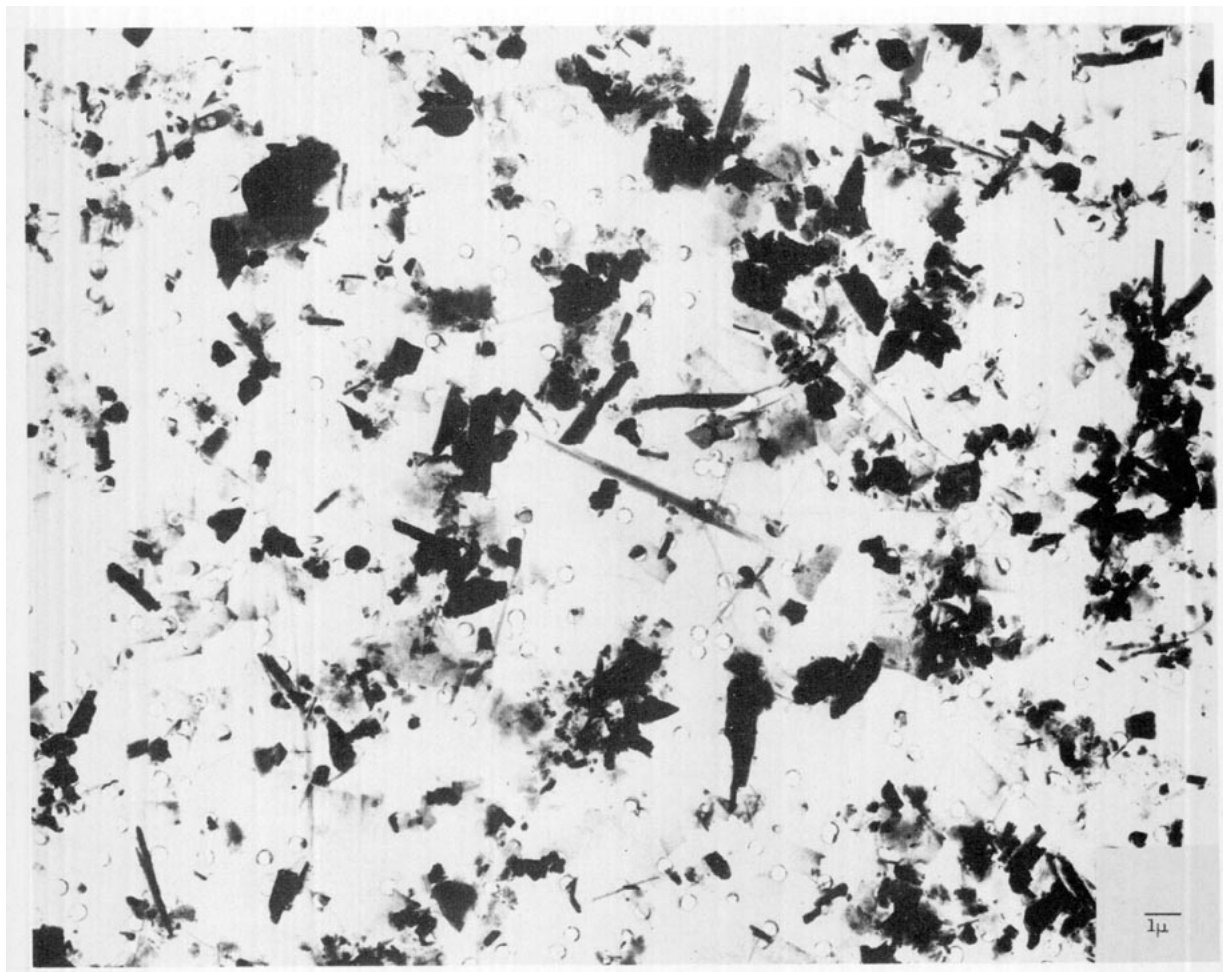


FIGURE 1. Fine fraction of debris from the mill tailings discharge. This sample was prepared after allowing a suspension of the tailings in water to settle for 20 min.

show higher magnification views of fibers present in the tailings. In some instances they are present as fiber bundles and have an appearance similar to chrysotile. Thus, the analysis of water systems based on the morphology of fibers alone can be misleading. In other instances, fibers have rectilinear morphology with 90° terminations typical of chain silicates and often exhibit the unique features of striations of electron opaque bands across the fiber diameter, as in Figure 3. In addition to the fibers, there is a wide variety of other nonfibrous mineral material.

Were this discharge confined to the immediate vicinity of Silver Bay, the problem would be one of localized site pollution. Unfortunately, this is not the case. Bottom currents

carry much of this material to Duluth, 60 miles southwest, which, along with other municipalities, draws its water directly from Lake Superior. Because of the past high purity of Lake Superior, the water is unfiltered prior to distribution and use. Figure 4 shows a sample of material filtered from 5×10^{-5} cm³ of Duluth water. Present in this sample are numerous amphibole fibers, amphibole pieces, other crystalline material, and diatom fragments.

That these fibers, as well as those in the tailings, were amphibole was verified by using the techniques of electron diffraction. Figure 5 shows the pattern obtained from a fiber in the Duluth water system. Measurements of the periodicity of the pattern demonstrate unambiguously that the fiber is of the amphibole

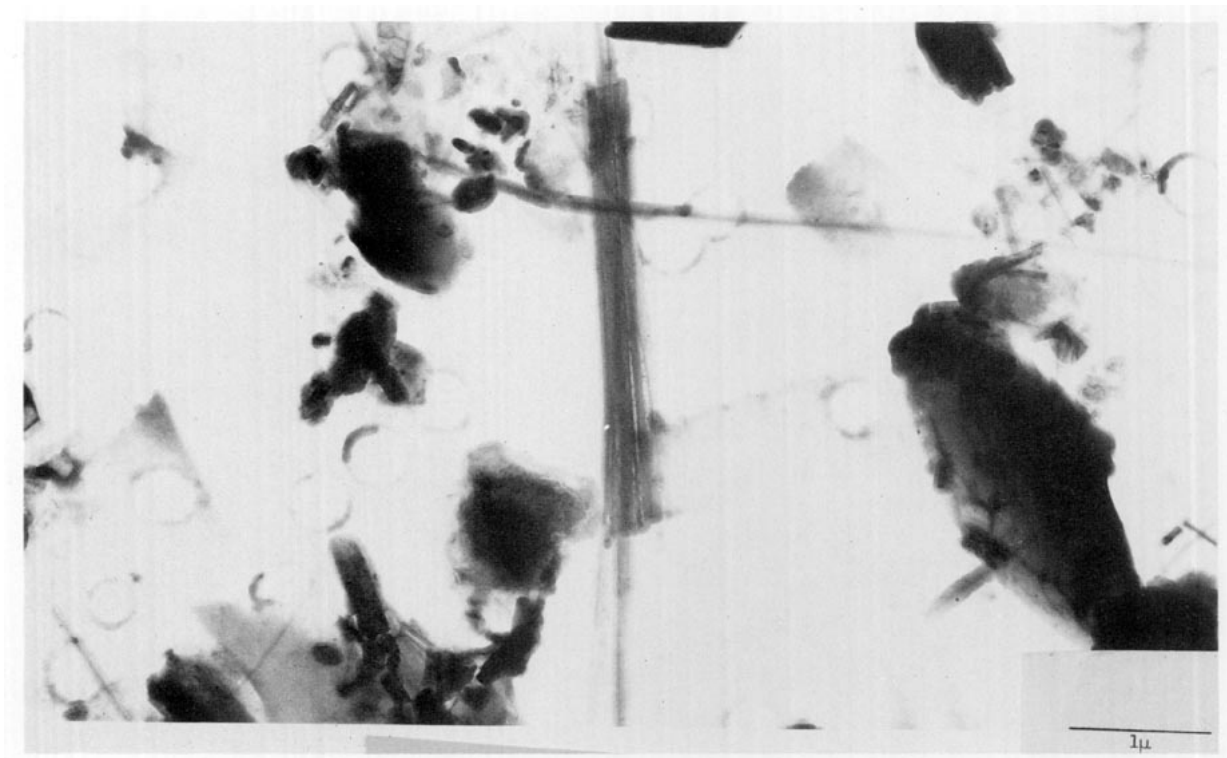


FIGURE 2. Higher magnification photograph of some of the fine fibers found in the discharge. While having the appearance of chrysotile asbestos, these fibers are, in fact, amphiboles.

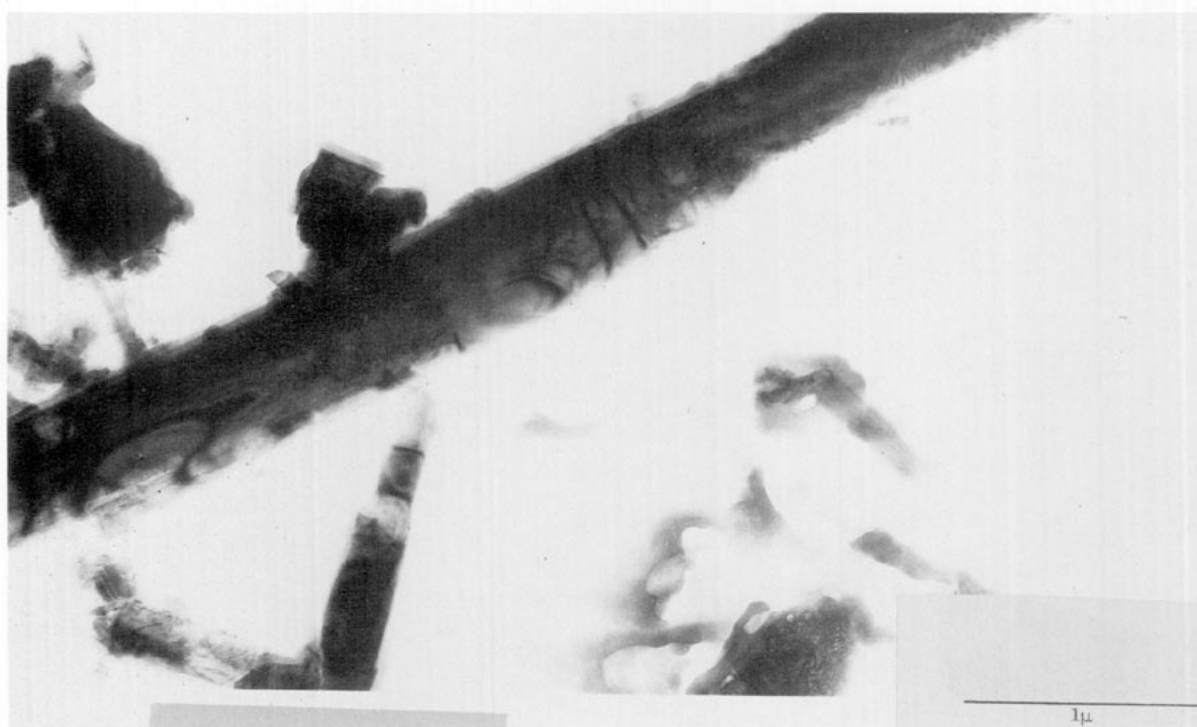


FIGURE 3. Single amphibole fiber found in the tailings discharge. The electron opaque striations seen here are commonly found in many of the discharge fibers.

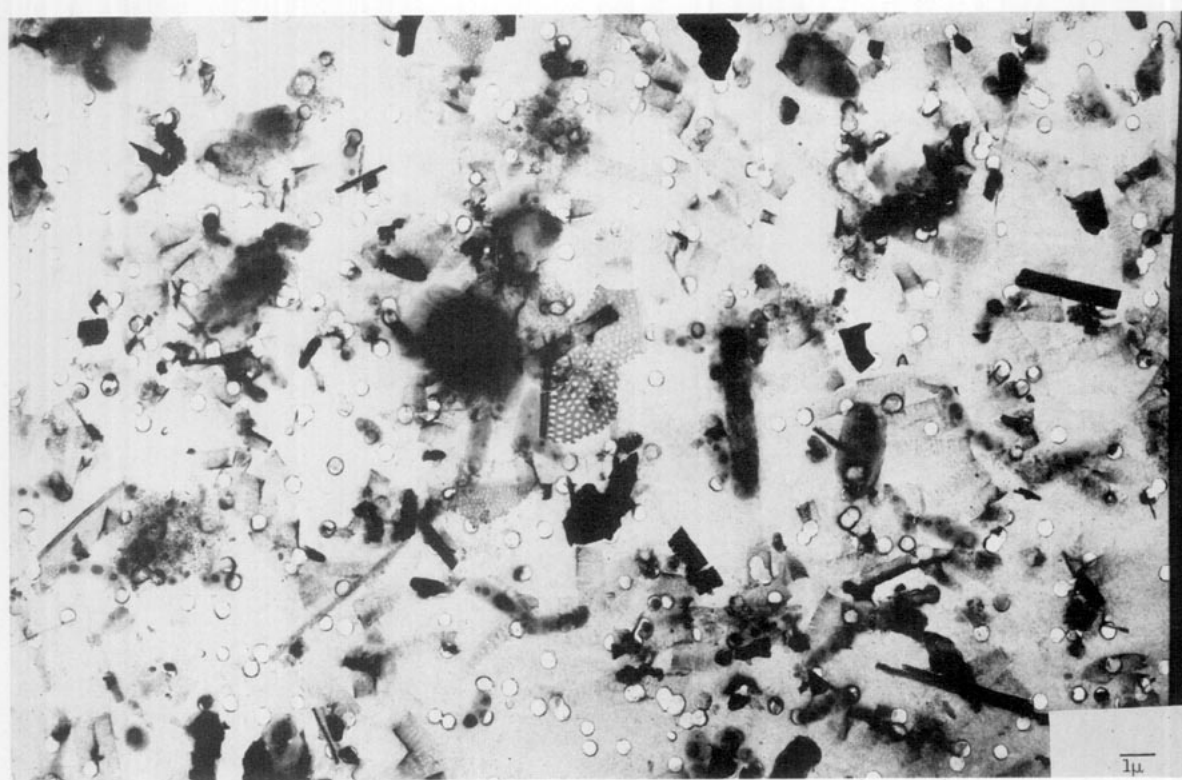


FIGURE 4. Filtered residue from 5×10^{-5} cm³ of Duluth water. Visible are numerous amphibole fibers, amphibole fibers, amphibole pieces, other crystalline material, and diatom fragments.

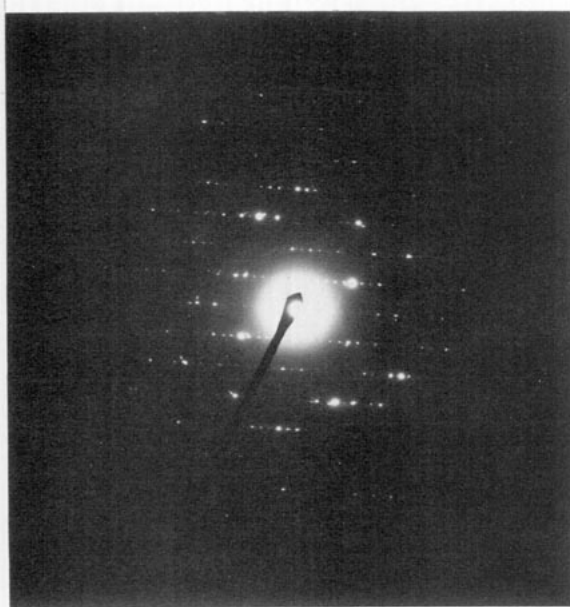


FIGURE 5. Electron diffraction pattern of a fiber found in the Duluth water system.

mineral class. A high magnification electron photomicrograph of the fiber, as shown in Figure 6, shows striations similar to those of fibers in the tailings. Often, as here, fibers are present in the water system with cleavage planes less defined than those in the tailings. This is to be expected from the presence in the water of some of these fibers over long periods of time.

Samples for analysis were prepared by filtering 10–20 cm³ of water obtained from municipal distribution systems through 2 cm² of Nuclepore filter. The filter, which had 0.4 μm diameter pores, was used because it provided a flat surface on which the mineral debris in the lake could be deposited. Following filtration, the filter was dried and coated with carbon to fix in place the various deposited materials. A small section of the filter was then cut and placed deposit-side-down on an electron microscope grid which, in turn, had been provided with a Formvar film. Chloroform fumes were then used to dissolve the Nuclepore filter, leaving the par-



FIGURE 6. High magnification view of an amphibole found in Duluth water having striations similar to those of fibers found in the tailings.

ticles imbedded in the carbon film on the microscope grid. Filters having fibrous or irregular surfaces were found to be unsuitable, as fibers could be deposited at various depths within the filter. During carbon coating such fibers were not trapped in the carbon film and would be subsequently lost. Depending upon the circumstances, the amount lost could approach 90% of the very fine material of interest.

A second preparation method, particularly suitable when the fibers of interest constitute only a small portion of the mineral material present, is a rub-out technique. Here, the filter and collected material are oxidized at low temperature in an activated oxygen asher. The debris is dispersed by grinding or application of ultrasonic energy and imbedded in a nitrocellulose film, a portion of which is mounted on the electron microscope grid. Each technique was utilized in the analyses of water systems and comparable results were obtained.

Typical length and width distributions of the verified amphibole fibers in the Duluth water

system are shown in Figures 7 and 8. Approximately 98% of the fibers are under 5 μm in length, with the most probable length being about 0.7 μm . Of those fibers verified as

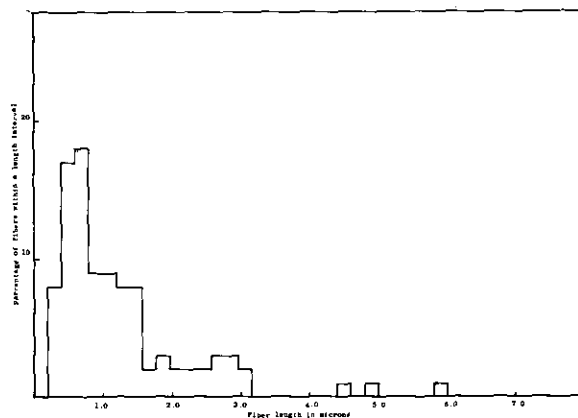


FIGURE 7. Typical length distribution of fibers found in the Duluth water system. The fibers were identified as amphibole on the basis of their electron diffraction pattern. The length distribution of fibers too small for visual electron diffraction analysis is similar. These small fibers have virtually identical x-ray emission spectra.

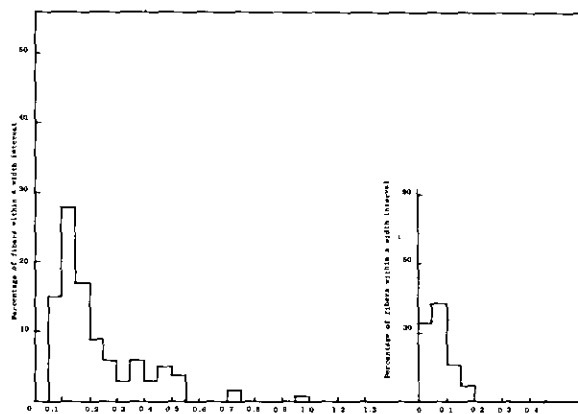


FIGURE 8. Typical width distribution of certified amphibole fibers from samples of Duluth water. The fibers were identified as amphibole fibers as on the basis of their electron diffraction pattern. Also shown (right) is the distribution of fibers too small for visual verification as amphibole minerals by electron diffraction. These fibers have x-ray emission characteristics virtually identical to those of larger fibers certified as amphiboles. The larger and the smaller fibers are found in roughly equal numbers.

amphibole by electron diffraction techniques, the most probable width is 0.15 μm .

Photographic electron diffraction techniques

and electron microprobe analysis were performed on random fibers having diameters sufficiently thin that inadequate visual diffraction patterns were obtained on the viewing screen. In all cases, these fine fibers were determined to be amphibole and in some samples equalled the number of fibers on which one could obtain visually (as opposed to photographically) verified amphibole patterns.

The results of our analyses of asbestos minerals in the Duluth water system are shown in Table 1 and indicate that the concentrations of verified amphibole mineral fibers range from approximately 20×10^6 to 75×10^6 fibers/l. water. These fiber concentrations correspond to approximately 5–30 μg amphibole fibers/l. water. The concentration of fibers was found to be similar throughout the Duluth water system, which consisted of three main reservoirs located at different altitudes within the city. The amphibole fiber concentrations listed here are those of fibers that were positively identified by electron diffraction techniques. Supplementary data suggest that concentrations are underestimated by at least a factor of two.

Table 1. The mass and number of amphibole fibers in the water system of Duluth.

Reservoir system	Analysis procedure	Concentration of amphibole fibers, $\mu\text{g/l.}$	Number of amphibole fibers/l. $\times 10^{-6}$
Lower	Rub-out	27	74
	Direct transfer	10	31
Middle	Rub-out	2.7	25
	Direct transfer	6.6	17
Upper	Rub-out	11	24
	SEM data		20 (11 C-A-G) ^a
System Intake	Direct	16	46
	transfer		57
	SEM data		(34 C-A-G) ^a
	Rub-out	20	60

^aThis quantity of fibers was found to be in the cummingtonite-amosite-grunerite series by utilizing the microprobe capability of a scanning electron microscope.

Numerous amphibole fibers, either too thin or too thick to provide unambiguous visual diffraction patterns, are not included in these tabulations.

A mass concentration of amphibole fibers was estimated utilizing measured fiber lengths, widths and fiber depths obtained from averages of an overestimate and an underestimate of the unobservable dimensions. The overestimate was to assume a third dimension equal to the measured width. The underestimate was to assume an average depth of $0.15 \mu\text{m}$, the peak in the width distribution. Masses calculated by each of these techniques usually differed only by a factor of two or three. (The average difference was 2.6.)

An analysis of the water from other municipal systems is provided in Table 2. It demonstrates that considerably fewer fibers were present in the water system of Superior, Wisconsin, the neighboring city of Duluth, and one which draws only a portion of its water from Lake Superior. Even there, however, the concentration of amphibole fibers was $4 \times 10^6/\text{l.}$ water. In a similar analysis of water from New York City and from Grand Marais, Minnesota, which is up-current from Silver Bay, no amphibole fibers were detected.

Table 2. The mass and number of amphibole fibers in the water systems of other cities.

Reservoir system	Analysis procedure	Concentration of amphibole fibers, $\mu\text{g/l.}$	Number of amphibole fibers/l. $\times 10^{-6}$
Superior, Wisconsin	Rub-out	1.4	4
New York City	Rub-out	N.D.	
Grand Marais, Minnesota	Rub-out	N.D.	

To further specify the nature of the mineral fibers in these water systems, electron microprobe analysis was performed. Here, the x-ray spectra generated by the electron bombardment of particular fibers are recorded and compared with standard spectra similarly generated from known mineral species. Figure 9

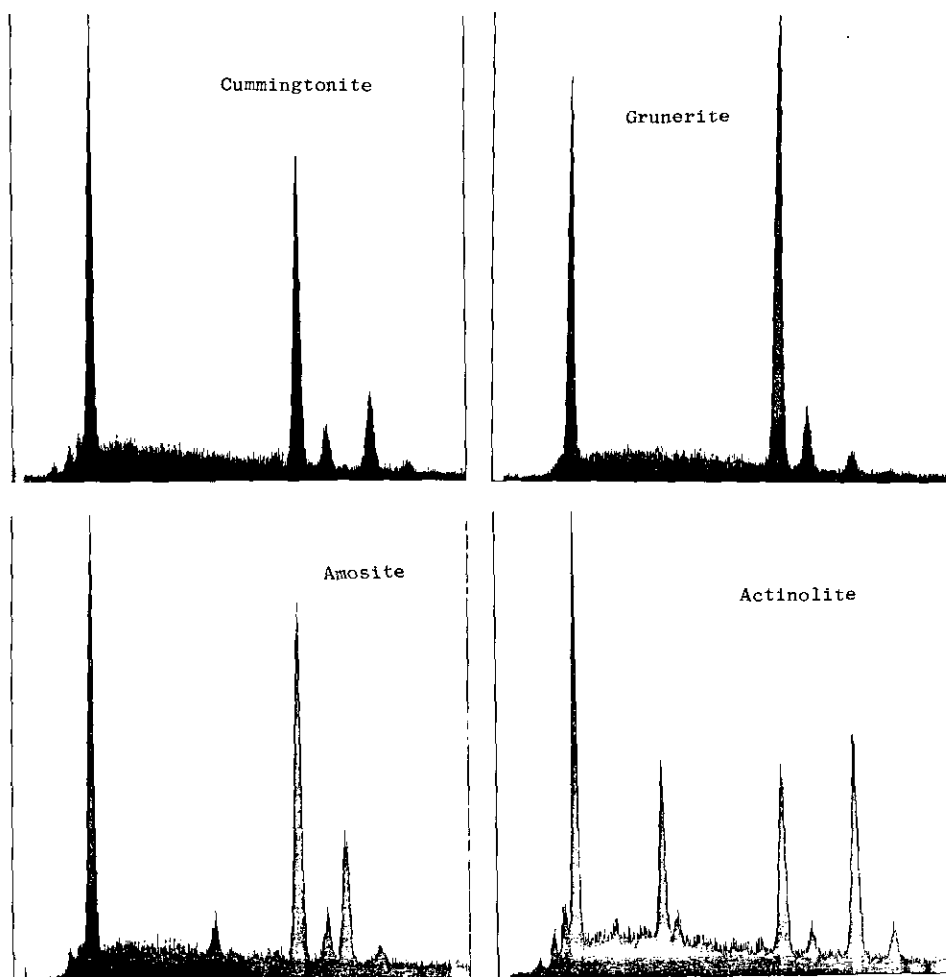


FIGURE 9. X-ray emission spectra of four common amphibole minerals. Present in each are high peaks attributable to silicon and iron; smaller peaks due to magnesium, in the case of cummingtonite, and aluminum, magnesium, and calcium in the case of actinolite. The two righthand peaks in each spectrum are the K- α and K- β lines of either nickel or copper present in the supporting grid structure.

shows such spectra obtained from three common mineral species found in the Duluth water system, along with that of amosite asbestos. As can be seen, cummingtonite, grunerite, and amosite have similar spectra, differing only in the relative quantities of iron and magnesium. Actinolite, on the other hand, differs significantly from the others due to the presence of a calcium peak. Data from spectra such as these can be plotted on a ternary diagram in which the percentages of iron, silicon and magnesium (multiplied by ten) are plotted. Such a plot for common amphibole minerals is shown in Figure 10. Cummingtonite, grunerite, amosite, and actinolite overlap on this diagram

and are difficult to distinguish, one from another. If the same fibers are plotted on a diagram with iron, calcium, and aluminum as coordinate axes (Fig. 11), actinolite can be clearly separated from the other minerals and also from tremolite and hornblende. Table 3, shows the identification of a sample of the fibers found in the Duluth water system and in the tailings. Approximately 50–60% of the fibers are in the cummingtonite–grunerite series, with approximately 5% having the identical chemical composition of amosite asbestos. Approximately 20% are in the actinolite tremolite series, with 2–4% consisting of hornblende. Of the amphibole fibers, approximately 20% had

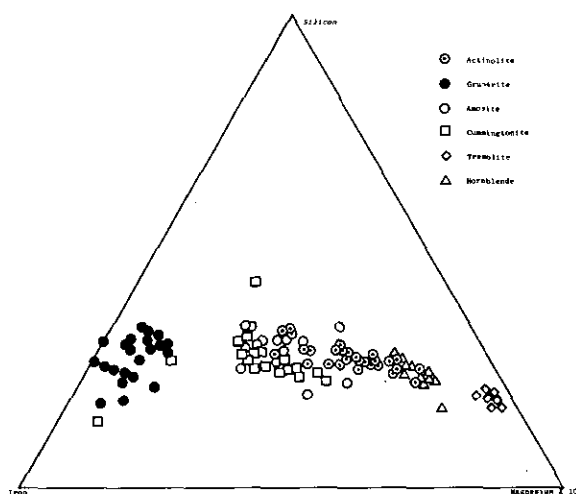


FIGURE 10. Ternary diagram showing the various percentages of iron, magnesium, and silicon for six amphibole minerals: (●) actinolite; (●) grunerite; (○) amosite; (□) cummingtonite; (◇) tremolite; (Δ) hornblende.

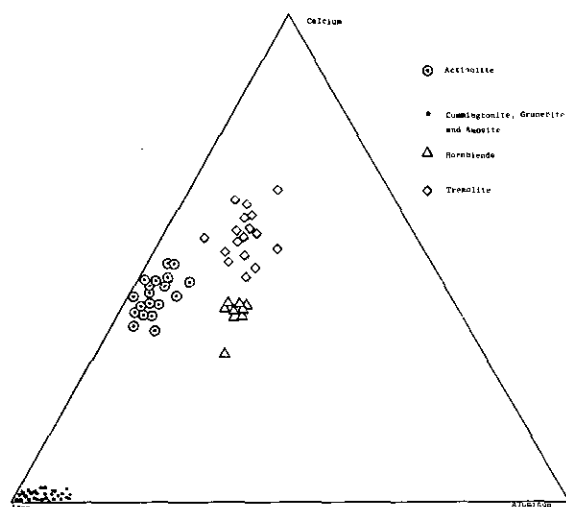


FIGURE 11. Ternary diagram showing the percentages of iron, magnesium, and calcium for six amphibole minerals: (●) actinolite; (●) cummingtonite, grunerite, and amosite; (Δ) hornblende; (◇) tremolite.

compositions that would not allow them to be assigned to any of the above minerals.

In summary, this work illustrates that a wide variety of analysis techniques is necessary if one wishes to have unique identification of the mineral species in water systems. Morphology

Table 3. Emission characteristics of fibers in Duluth water system and reserve tailings discharges.

Fiber	No. (%) of fibers	
	Duluth	Tailings
Cummingtonite-grunerite	90 (47)	56 (62)
(Amosite)	(8) (4)	(6) (7)
Actinolite-tremolite	43 (22)	18 (20)
Hornblende	8 (4)	2 (2)
Other	51 (27)	15 (16)
Total number of fibers analyzed	192	91

alone would be insufficient. Electron diffraction techniques would give only limited information. Only by utilizing the full spectrum of the available analytical techniques of electron microbeam analysis, transmission electron microscopy, electron diffraction and electron microprobe analysis, is one able to obtain unambiguous identification of water system fiber contamination.

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